The origin and the meaning of the little p in pH

The concept of pH as an expression for the hydrogen-ion concentration was proposed in two papers ^{1,2} in 1909 by the Danish chemist Søren Peter Lauritz Sørensen, director of the Chemical Department of the Carlsberg Laboratories between 1901 and 1938. The letter H obviously stands for H⁺-ion, but what does the little p mean?

My interest in this p was triggered by a question from a friend. He was an economist in the dairy industry and had visited dairies and heard about the importance of pH in cheese production. Although not a natural scientist, he knew that the H had something to do with the acidity (the H⁺ concentration), but what about the p? I could not answer his question immediately, but was quite certain that at home I had the necessary material to solve the problem.

My father completed his doctoral thesis at the Carlsberg Laboratory in the period 1931–1934. Under Sørensen's influence he became interested in the importance of pH in biology, and my mother had bound him a copy of 'Études Enzymatiques. II. Sur la mesure et l'importance de la concentration des ions hydrogène dans les réactions enzymatiques'. It was here that I expected to find the solution to the origin and the meaning of the little p.

However, as will appear from the following, my conclusion deviates radically from other published opinions on the meaning of the little p in pH.

A false association?

In Sørensen's papers from 1909 (or later) there is no mention of the meaning of the p: Sørensen denotes pH as 'exposant des ions hydrogène' or 'Wasserstoffionenexponent'. This is also acknowledged by Clark in 1922 (Ref. 3):

Although Sørensen has not revealed the considerations which led to the choice of the letter P in his symbol, we might regard P as suggesting the potential (intensity) factor of the acidity as described above.

What is alluded to here by Clark, is that the potential of a hydrogen electrode is a linear function of $-\log[H^+]$, but this is Clark's personal interpretation of the p. However, in the next edition of his book⁴, Clark states that

..the association of the words 'potenz' and 'puissance' with pH arose in a totally different manner. and he then quotes from Sørensen's 1909 text¹:

...., la grandeur de la concentration des ions hydrogène s'exprime par le facteur de normalité de la solution par rapport aux ions hydrogène, facteur indiqué d'une puissancel negative de 10.

Dans tous les cas traités dans le présent memoire

.... le facteur de normalité de la solution sous le rapport des ions hydrogène ou, en d'autres terme, le nombre d'atomes-grammes d'ions hydrogène par litre est plus petit que 1 et peut être posé égal a 10-p, où pour le nombre p je propose le nom d'exposant des ions hydrogène et la désignation pH. Par exposant des ions hydrogène (pH+) d'une solution, nous entendons donc le logarithm Brigg de la valeur réciproque du facteur de normalité de la solution relativement aux ions hydrogène.

[Clark's footnote: ¹ Potenz' in the German translation, i.e., power (mathematical)].

It should be said that Clark is not alone in making these 'associations'. Examples from reviews, textbooks and other sources concerning the meaning of the little p are listed in Table 1. The words power and potential feature in many of these.

Examining Sørensen's original article, the complete paragraph on p.4 in Sørensen's paper¹ (Fig. 1), from which the first part of Clark's quote originates, says nothing about the origin or the meaning of the little p (note that the second half of

the paragraph in Fig. 1 is absent in Clark's quotation). The second part of Clark's quotation is from p.28 in Sørensen's text (Fig. 2). Clark does not mention the 24 pages that separate the two parts of his quotation, and it is also important to note that just prior to the second part of Clark's quote there is an equation in Sørensen's paper that contains both an electromotoric force (π_n) and a concentration (C_p) with the subscript p (Fig. 2). Furthermore, the sentence '..., C_n – qui signifie, comme nous l'avons dit,...' is omitted in Clark's version. By these changes and omissions, Clark has created an association between 'puissance negative de 10' and 'peut être posé égal a 10^{-p} ', which is completely absent in the original text.

Minding the p's and q's

Let us therefore have a closer look at how p originates in Sørensen's papers^{1,2}. An essential and very important theme in Sørensen's work is the elaboration of an accurate, electrometric method for the determination of the H⁺-ion concentration. For this purpose he uses a pile consisting of a calomel electrode (which has a 'fixed' electrode potential) and a hydrogen electrode, the potential of which depends on the H⁺-ion concentration of the electrode solution. The procedure is described in Fig. 3. Equation (I) contains four variables, but π_{p} and π_{q} can be measured. Sørensen now chooses to set $C_q = C_0 = 1$, and $\pi_q = \pi_0$. Because K has been determined as 0.0577, equation (I) has hereby changed to:

$$\begin{split} \pi_0 &= \pi_{\rm p} - 0.0577 \log(C_0/C_{\rm p}) = \\ \pi_{\rm p} &= 0.0577 \log(1/C_{\rm p}) \end{split} \tag{II}$$

To determine π_0 , Sørensen prepares a series of diluted hydrochloric-acid solutions with known concentrations. Through the values for degree of dissociation and conductance established by Arrhenius and Kohlrauch (see Ref. 1, pp. 23–28) the exact concentration of H⁺-ion (C_p) in these solutions is calculated, and a number of corresponding values for C_p and π_p are determined. For each set a

Table 1. False associations regarding the meaning of p in pH.	
Quote	Refs
p is the initial letter of the words Potenz, puissance, power that they be represented by the symbol pH. (p = power)pH. The H stood for 'hydrogen ion' and the p for ' puissance ' (French), ' Potenz ' (German)	5 6 7
or 'power'den pH-Wert (lat. pondus hydrogenii)pH hvor H står for hydrogenion og p for potens (latin: potentia hydrogenii)pH is short for potential of Hydrogenoperatortecknet p, som betyder 'den negative logarithme'	8 9 10 11

Par conséquent, la grandeur de la concentration des ions hydrogène s'exprime par le facteur de normalité de la solution par rapport aux ions hydrogène, facteur indiqué sous la forme d'une puissance négative de 10. Pour les détails, je renvoie mes lecteurs à un autre chapitre (v. p. 28); je me bornerai à mentionner ici que la valeur numérique de l'exposant sera désignée par p_H et appelée exposant des ions hydrogène.

Figure 1

Quote from Sørensen's paper¹, p. 4. The definition of pH. (Note that pH is hereby defined as the negative logarithm to the factor, by which 1 N must be multiplied to obtain the H+-ion concentration, and not as the negative logarithm to the H+-ion concentration – units are not allowed under the log sign!).

Si nous introduisons cette valeur de π_0 dans l'équation (II) (p. 23), celle-ci revêtira la forme suivante:

$$\pi_{\rm p} = 0.3377 + 0.0577 \log \frac{I}{C_{\rm p}}$$
 (III)

 $\pi_{\rm p}=0.3377+0.0577\,\log\frac{1}{C_{\rm p}} \eqno(III)$ Dans tous les cas traités dans le présent mémoire, $C_{\rm p}$ — qui signifie, comme nous l'avons dit, le facteur de normalité de la solution sous le rapport des ions hydrogène ou, en d'autres termes, le nombre d'atomes-grammes d'ions hydrogène par litre - est plus petit que I et peut être posé égal à 10-p, où pour le nombre p je propose le nom d'exposant des ions hydrogène et la désignation p_H. Par exposant des ions hydrogène (p+) d'une solution, nous entendons donc le logarithme Brigg de la valeur réciproque du facteur de normalité de la solution relativement aux ions hydrogène1).

Figure 2

Quote from Sørensen's paper¹, p. 28. This also shows how C_p or 10^{-p} (the H⁺-concentration/ 1N; see Fig. 1) can be determined electrometrically. See text and Fig. 3 for derivation of equation III.

value for π_0 is calculated by equation (II), and as π_0 is found to be independent of C_p , the average value (= 0.3377) is inserted into equation (II), resulting in equation (III) (see Fig. 2). By measurement of π_p , the unknown H^+ -ion concentration, C_p^{p} or 10^{-p} , can now be determined.

Conclusion

Thus, it seems that the little p in pH originates simply as a consequence of Sørensen's arbitrary choice of the letters p and q for the two solutions in his initial explanation of the electrometric method (Fig. 3). By choosing solution q to have the H⁺-ion concentration 1, the unknown

b. Détermination de π_0 .

Désignons par π_p la force électromotrice d'une pile composée d'une électrode au calomel plongée dans une solution norm. au 10° de chlorure de potassium et, d'autre part, d'une électrode en platine hydrogéné placée dans une liqueur électrolyte dont la concentration en ions hydrogène, exprimée avec une solution normale d'ions hydrogène comme unité, est de C_p (= 10^{-p}); si alors nous désignons par π_q et C_q (= 10^{-q}) les quantités correspondantes d'une pile analogue, on aura

$$\pi_p - \pi_q = K \log \frac{C_q}{C_p},$$
 (I)

Figure 3

Quote from Sørensen's paper¹, p.22. Introductory explanation to the electrometric determination of the H⁺-ion concentration. The choice of the letters p and q to denote two alternative possibilities, items or situations were (and still are) quite common in mathematics^{12,13} and in other natural sciences, for example, genetics^{14,15}.

concentration of H⁺-ions gets the concentration symbol C_p or 10^{-p} , and Sørensen proposes '...pour le nombre p...le nom d'exposant des ions hydrogène et la désignation p^+_{H} .

And maybe it is therefore as H.C. Andersen says in the fairy tale *The Nightingale*¹⁶:

'What's that?' exclaimed the Emperor. 'I don't know the Nightingale at all! Is there such a bird in my empire, and even in my garden? I've never heard of that. To think that I should have to learn such a thing for the first time from books!' And hereupon he called his cavalier. This cavalier was so grand that if anyone lower in rank than himself dared to speak to him, or ask him any question, he answered nothing but 'P!' – and that meant nothing.

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References

- 1 Sørensen, S.P.L. (1909) Études enzymatiques. II. Sur la mesure et l'importance de la concentration des ions hydrogène dans les réactions enzymatiques. Compt. rend. du Lab. de Carlsberg 8, 1–168
- 2 Sørensen, S.P.L. (1909) Enzymstudien. II. Mitteilung. Über die Messung und die Bedeutung der Wasserstoffionenkoncentration bei enzymatischen Prozessen. *Biochem. Zeitschr.* 21, 131–304, and 22, 352–356
- 3 Clark, W.M. (1922) The Determination of Hydrogen Ions (2nd edn), p. 35, Williams & Wilkins Company
- 4 Clark, W.M. (1928) The Determination of Hydrogen lons (3rd edn), p. 36, Ballière, Tindall & Cox
- 5 Bates, R.G. (1973) Determination of pH, Theory and Practice, pp. 17–21, John Wiley & Sons
 6 Szabadváry, F. and Oesper, R.E. (1964) Development
- of the pH Concept. A historical survey. *J. Chem. Education*, 41, 105–107

 Kolb, D. (1979) The pH Concept. *J. Chem. Education*, 56, 49–53
- 8 Jäckel, M. et al. (1988) Chemie Heute, Sekundarbereich II, p. 123, Schrode Schulbuchverlag GMB 9 Andersen, E.S. and Parbo, H. (1988) Kemi i Perspektiv,
- 1, p. 110, Gyldendal
- 10 Kristiansen, J. (1999) A pHenomenal success. The Brew. The Magazine for the Carlsberg Group, 2, 8 11 Hägg, G. (1966) Allmän och oorganisk kemi, 4. uppl.,
- p. 39 and 311, Almqvist & Wiksell 12 Courant, R. (1950) Differential and Integral Calculus I,
- 2nd ed., p. 7, Blackie & Son Limited 13 Thomas, G.B., Jr (1972) Calculus and Analytical Geometry, pp. 863 and 904, Addison-Wesley Publishing Company
- 14 Pearson, K. (1904) Mathematical contributions to the theory of evolution. XII. On a generalised theory of alternative inheritance, with special reference to Mendel's laws. *Philos. Trans. A* 203, 53–86
- 15 Hardy, G.H. (1908) Mendelian proportions in a mixed population. *Science* 28, 49–50
- 16 Andersen, H.C. (1986) The Fairy Tales of Hans Christian Andersen. The Nightingale, p. 78, Weathervane Books

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